NHI Catalyst and Membrane Studies for Thermochemical Cycles at INL

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Project ID #
PDP28

Overview

Timeline

- Start dates
  - Catalyst work: June 2005
  - Membrane work: October 2005
- End dates (current workscope)
  - Both aspects: September 2007
- Percent complete: 50% (FY 2007 workscope)

Budget

- Total project funding
  - DOE share: 100%
- Funding received in FY06: $955K
- Funding for FY07: $750K

Barriers

- Barriers addressed
  - Centralized production pathway for hydrogen
  - Enabling technologies for nuclear assisted hydrogen production from water-splitting cycles

Partners

- Sandia National Laboratory
- General Atomics
- University of Sheffield, UK (informal)

Objectives

- **Develop enabling technologies for the Sulfur-Iodine (S-I) thermochemical cycle as a part of the Nuclear Hydrogen Initiative**
- **Apply these technologies to the Hybrid Sulfur (HyS) cycle and to other non-sulfur based thermochemical cycles**
- **Technologies include effective *catalysts* for chemical conversion and *membranes* for chemical separations**
- **These enabling technologies are needed to reduce cost and increase efficiency of the process**

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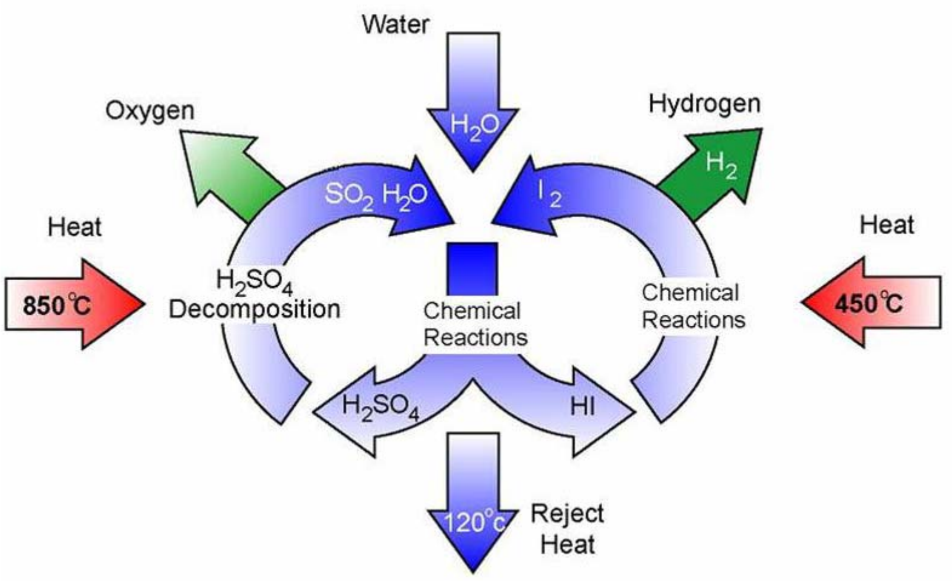
1. Approach-Catalysts

- Identify or develop highly active, stable catalysts for the S-I thermochemical cycle
- The S-I decomposition reactions present harsh environments for catalysts
- Catalysts explored for sulfuric acid decomposition included supported platinum group metals (PGMs) and complex metal oxides
- HI decomposition catalyst studies focused on activated carbons.



The Sulfur-Iodine cycle requires catalysts for both the H_2SO_4 and the HI decomposition reactions to achieve desired reaction rates at feasible temperatures.

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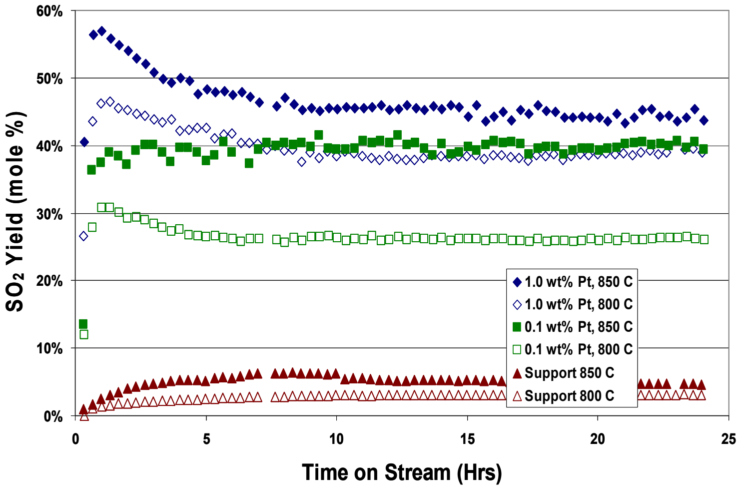
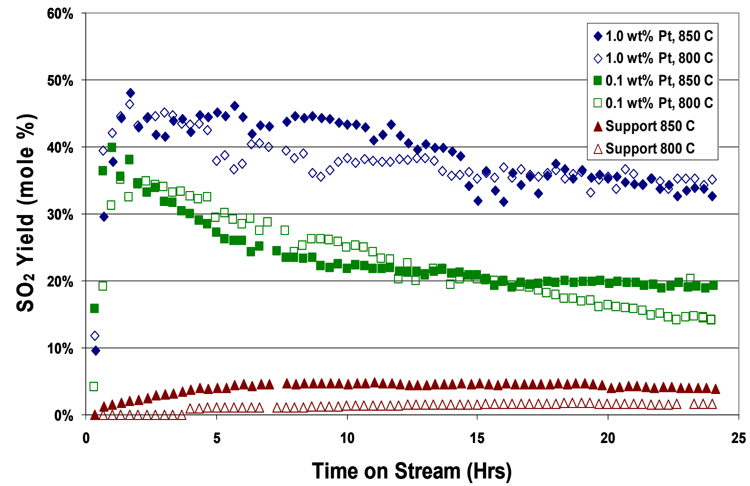
Technical Accomplishments - Catalysts

- Pt/TiO_2 has shown the best wide temperature range activity and stability for H_2SO_4 decomposition.
- Two commercial activated carbons, designed as catalyst carriers, were found to be active and stable for HI decomposition in 1 week continuous tests.
- The above catalysts were recommended for the S-I Integrated Laboratory Scale (ILS) project.
- Catalysts with higher stability for H_2SO_4 decomposition and higher activity for HI decomposition reactions are still needed.

H_2SO_4 Decomposition Catalysts





SO_2 yields over Pt/TiO_2 (left) and Pt/αAl_2O_3 (right) at 800 and 850 ºC.

- **Supports studied included: SiO_2, γ-Al_2O_3, ZrO_2, α-Al_2O_3 and TiO_2**
- **Initial activity increased with support BET area but stability decreased with BET support area**
- **Short term tests found Pt/TiO_2 to be the most stable**

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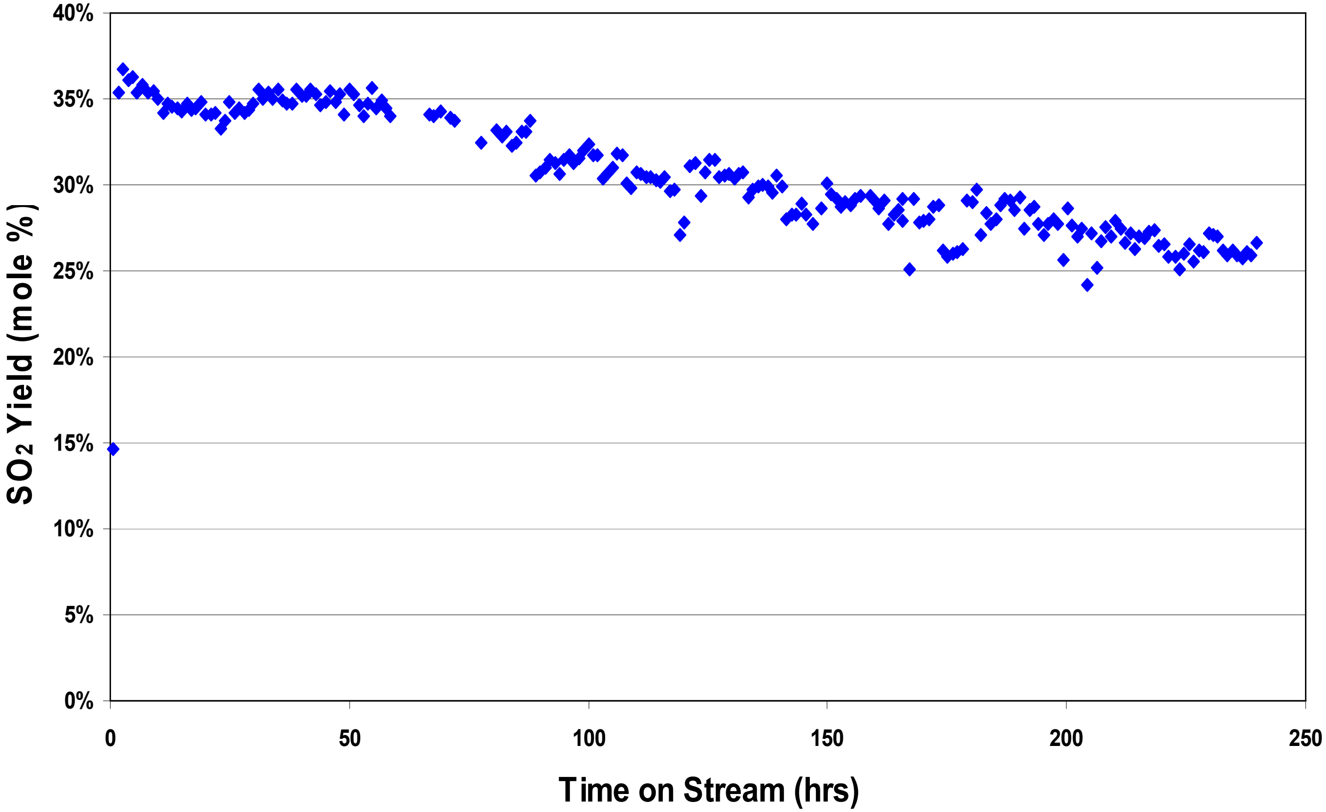
Long Term Pt/TiO_2 Activity at 820 ºC



0.1% Pt/TiO_2 catalyst lost about 28% of initial activity over 10 days of operation

Pt loss was approximately 30 wt %

Deactivation may be due to Pt sintering, oxidation, and vaporization

WHSV = 48 g acid/g cat./hr, 850°C

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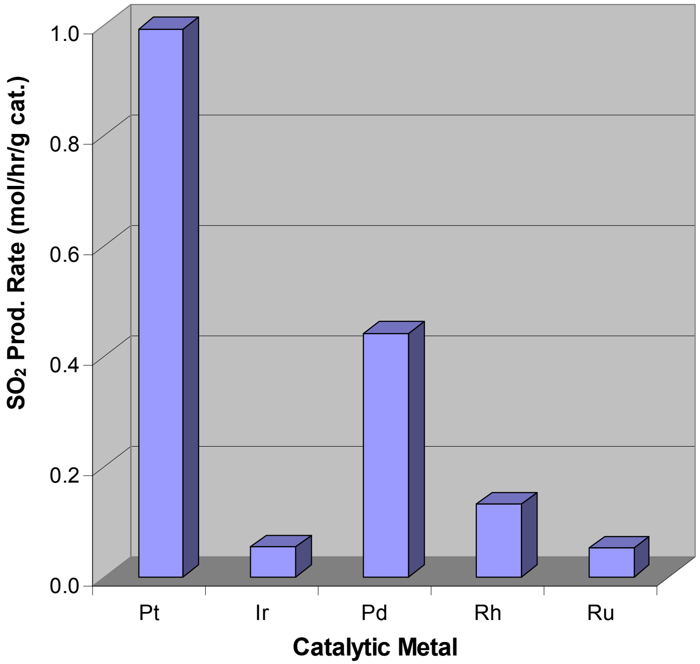
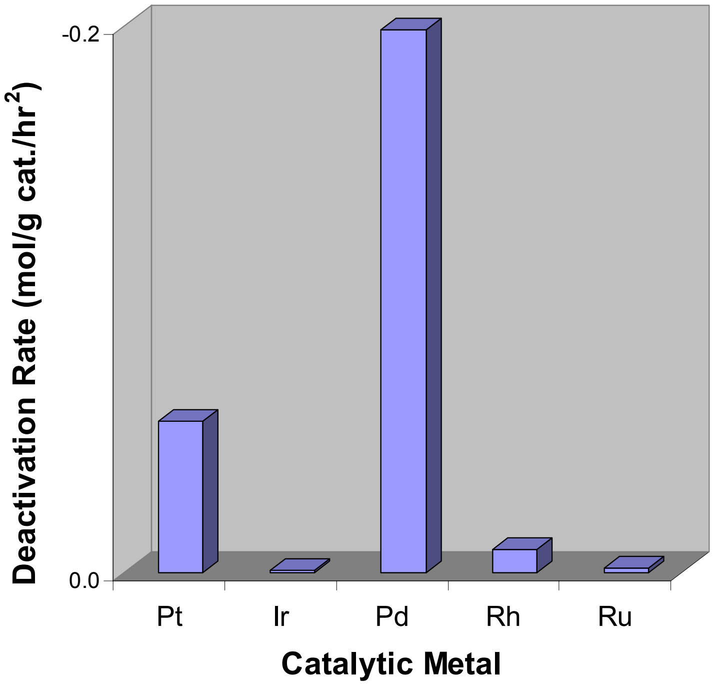
Activity and Stability of PGMs at 850°C



Initial reaction rate



Initial deactivation rate

- Pt and Pd had highest initial activity but also highest deactivation
- Ir, Ru, Rh were very stable but had low activity
- Could Pt mixed with Ir, Ru, or Rh have high activity and stability?

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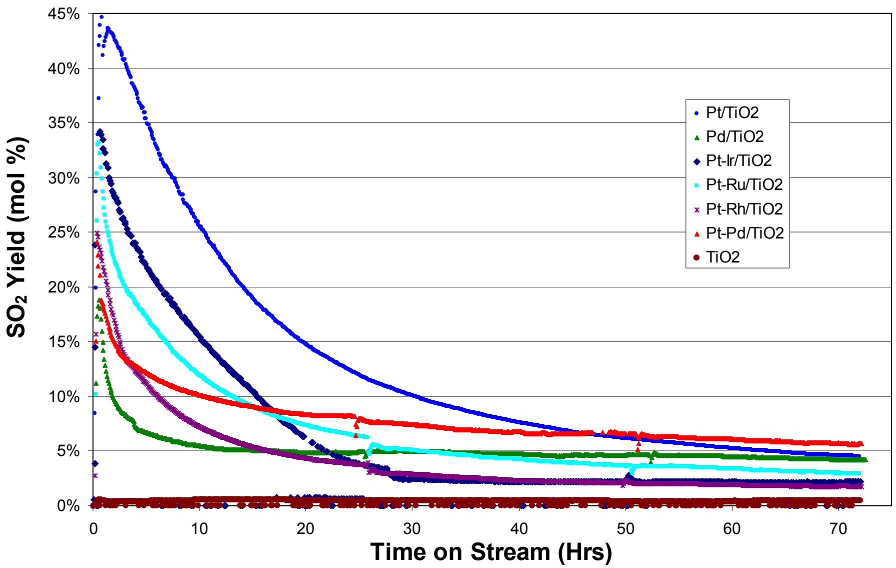
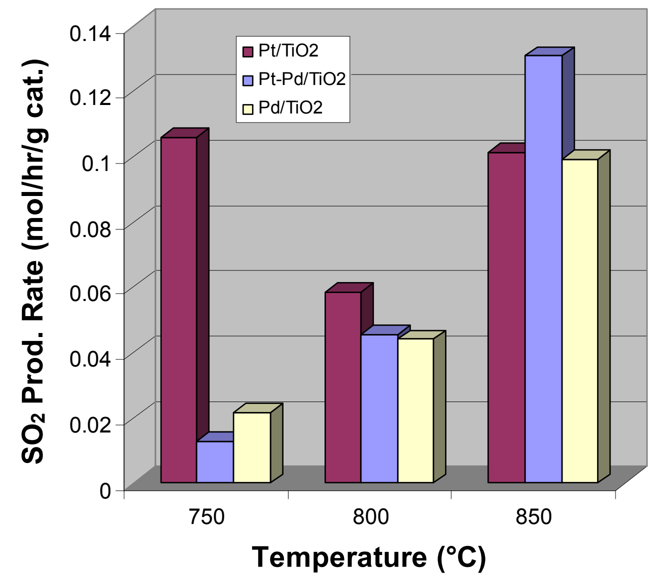
Activity and Stability of Mixed PGMs



Transient SO_2 rates at 850°C



End of run SO_2 rate (70-72 hrs)

- **Pt showed best activity over wide temperature range (750 to 850°C)**
- **Initial efforts mixing other PGMs with Pt did not stabilize catalyst**
- **Pt still preferred catalytic metal but improved stability still needed.**

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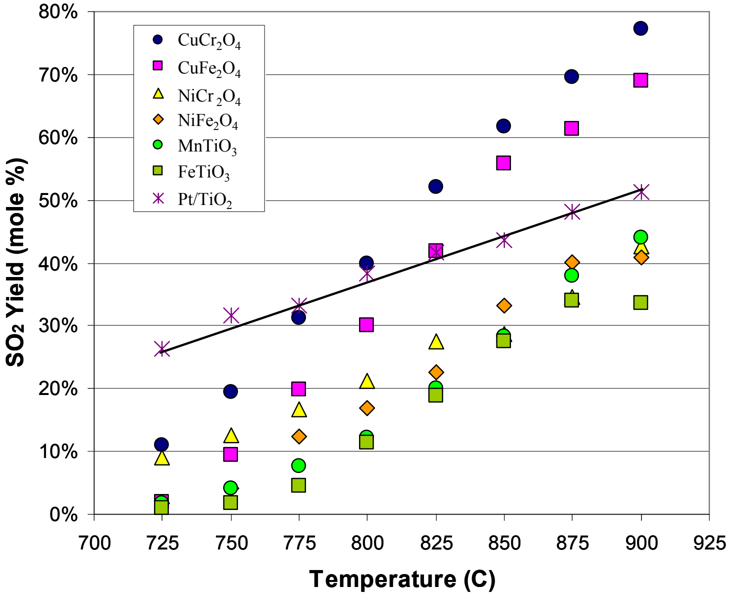
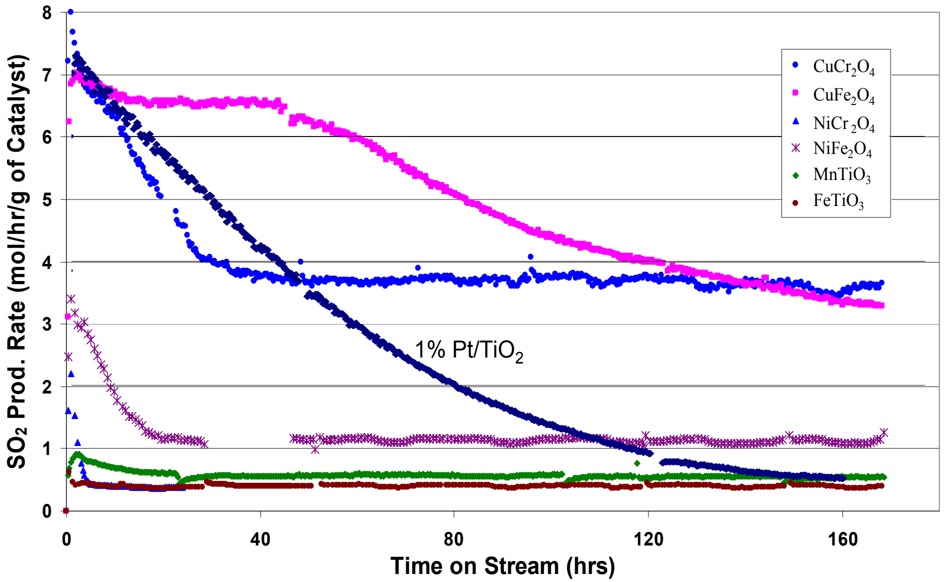
Complex Metal Oxide Catalysts



WHSV = 50 g acid/g cat./hr

SO_2 yields with temperature



WHSV = 2,000 g acid/g cat./hr, 850°C

Transient SO_2 production rate, 850°C

- **Some complex metal oxides had better activity than Pt above 825°C**
- **Stability of some complex metal oxides appeared promising**
- **Further exploration of complex metal oxides should be pursued**

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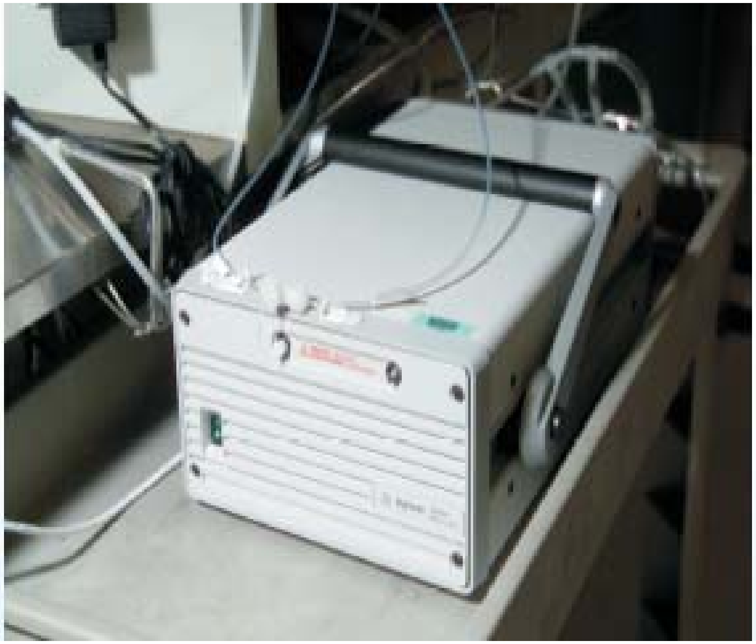
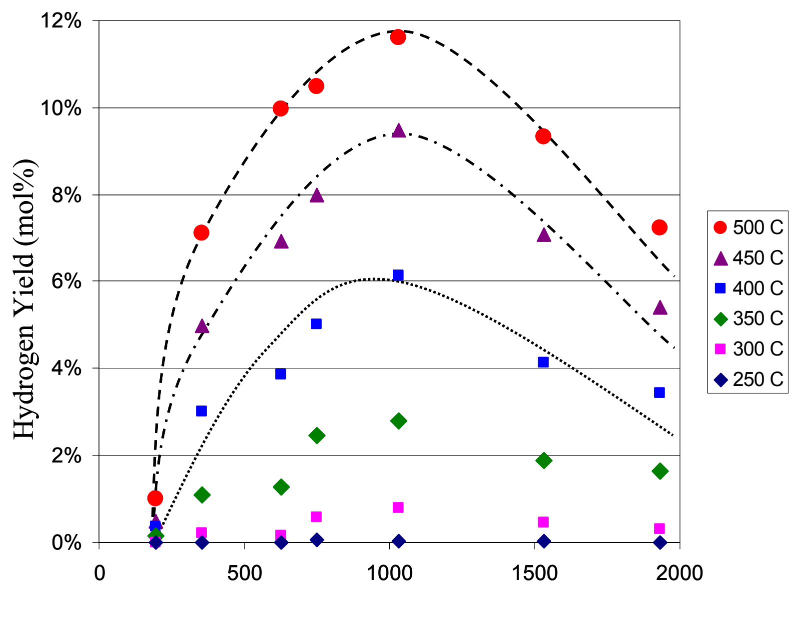
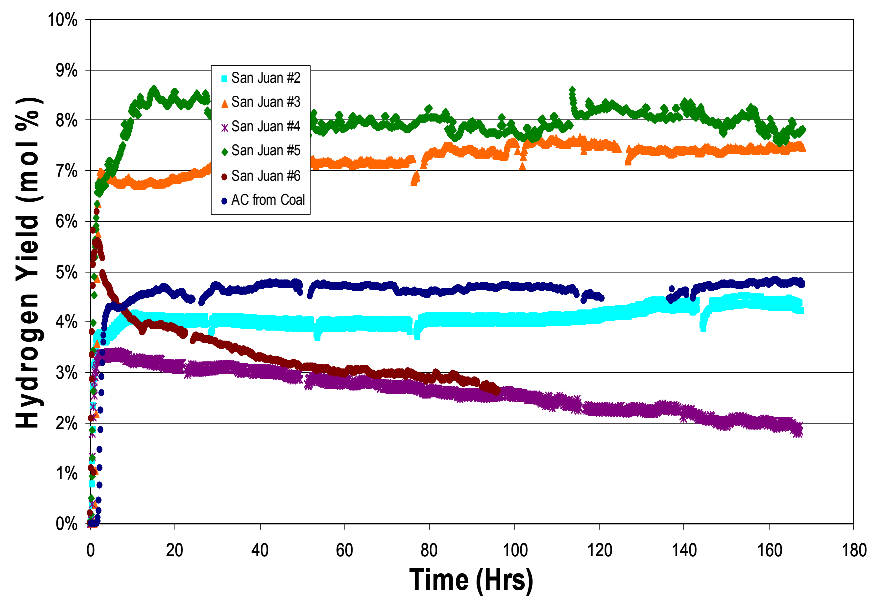
HI Decomposition Testing



- Atmospheric pressure, gas phase reaction
- Aqueous HI feed (55 wt% HI typical)

HI Decomposition over Activate Carbons





Temperature 475°C, WHSV = 130 g HI/g cat/hr

Surface area influence on H_2 yields

Transient H_2 yields

- **Most activated carbons relatively stable over one week testing**
- **Best activated carbon had moderate surface area of 1,000 m^2/g**
- **Work is in progress to understand influence of surface chemistry and morphology on catalytic activity and stability**

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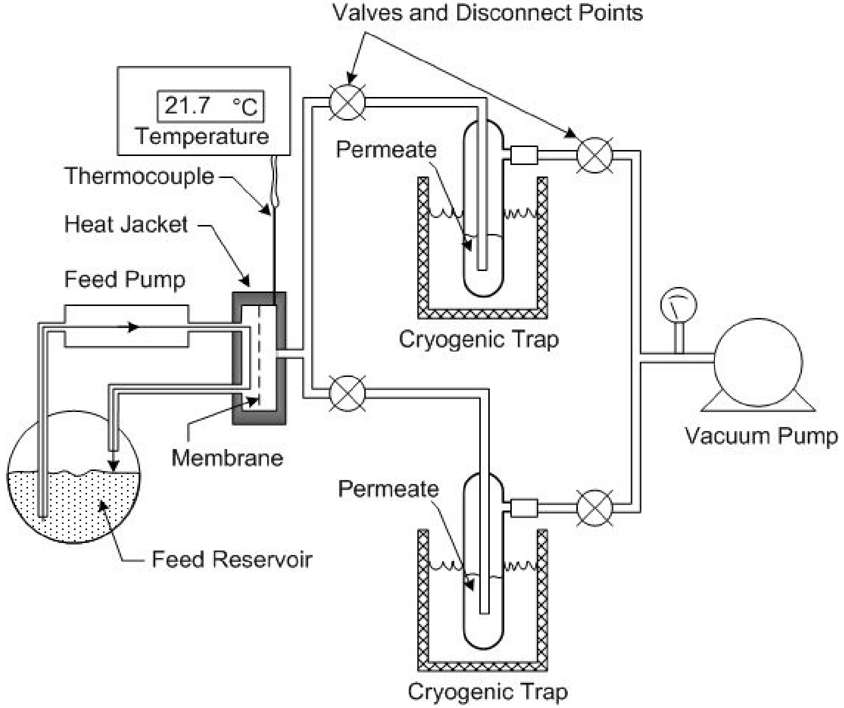
Future Work - Catalysts

- FY07 work scope (H_2SO_4 and HI experimental efforts)
  - Examine several more potential catalytic materials
  - Conduct long term testing of recommended ILS catalysts
- Upcoming key milestones:
  - Evaluate catalyst research needs for alternative cycles (report due June 1, 2007)
  - Evaluate membrane reactors for S-I cycle (report due June 1, 2007)
  - Perform long term tests on catalysts recommended for ILS (September 1, 2007)
- FY 08 proposed work scope
  - H_2SO_4 efforts should focus on improving Pt stability and explore complex metal oxides
  - HI work should focus on alternative catalytic materials, including polyoxometalates

2. Approach - Membranes

- Concentrate acid solutions relevant to the S-I cycle using pervaporation
- Desired temperature range = 120-350 ºC
- Advantages of Pervaporation:
  - Well-known commercial process
  - Uses solubility-selectivity as separation mechanism
  - Effectively breaks azeotropes
  - At the lower temperature end of the desired range, there are numerous membranes available; however few have the requisite temperature and chemical stability.
- Membranes studied: Nafion-117® and Nafion-112®
- Other separations
  - H_2 from HI and iodine (HI decomposition section)
  - SO_2 from O_2 (sulfuric acid decomposition products)



Membrane separations are accomplished using a pervaporation apparatus as shown above

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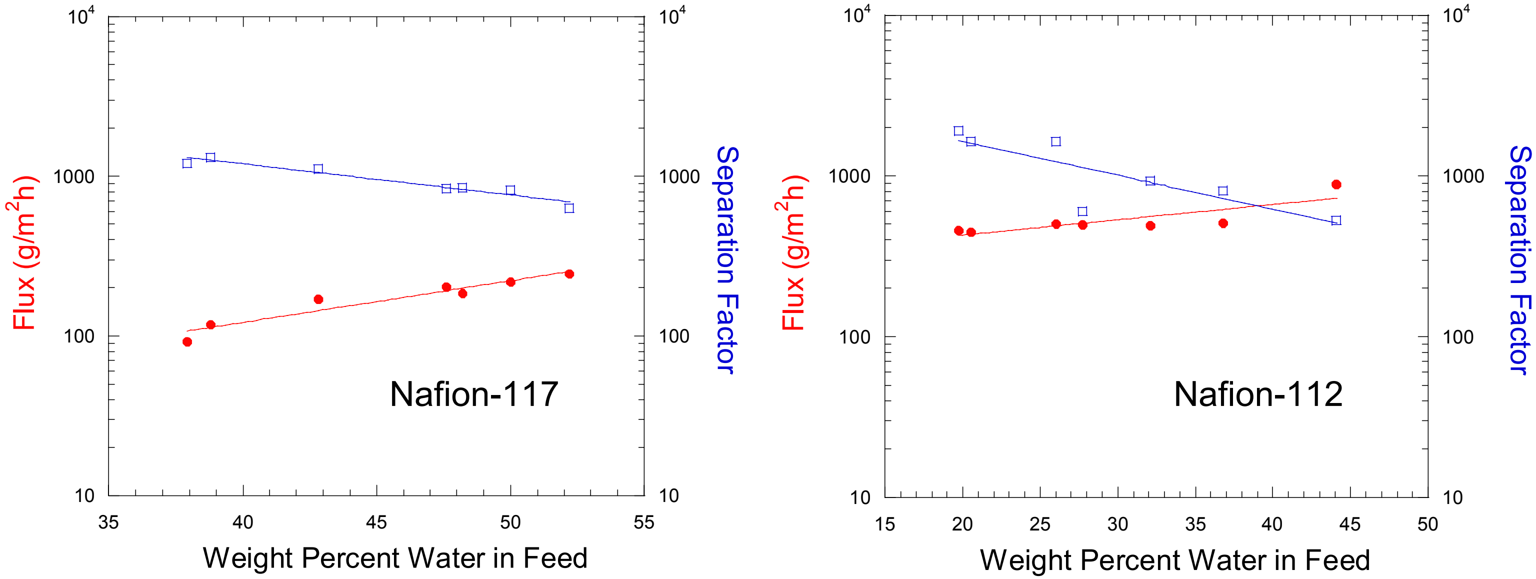
Technical Accomplishments - Membranes

- **During this reporting period, we have collected data that will allow for determination of the applicability of pervaporation separation processes to the S-I cycle**
- **The accomplishments of this project have directly addressed all project milestones and have provided a chemical separation capability for potential inclusion in the S-I integrated laboratory scale (ILS) demonstration**
- **During FY 2007, we have continued to characterize membrane performance for process parameters necessary to model membrane system performance under actual operating conditions – *this is important to determining whether pilot-plant scale systems should be constructed and tested***
- **Membrane performance for concentration of both hydriodic acid (HI) and sulfuric acid are commercially competitive**
- **No membrane degradation has been observed suggesting a long operational lifetime under S-I cycle conditions**

HI concentration



Flux (●) and separation factor (□) performance data for Nafion-117® (left) and Nafion-112® (right) at 134 ºC using an HI/water feed.

- **As a part of the S-I cycle, separation of the post-Bunsen reaction products is necessary to send HI to the decomposer**
- **Solutions of HI/water and HI/I_2/water were concentrated above the azeotropic concentration (57 % HI) at 134 ºC through the selective removal of water**
- **Membrane performance is provided in terms of flux through the membrane and separation factor**

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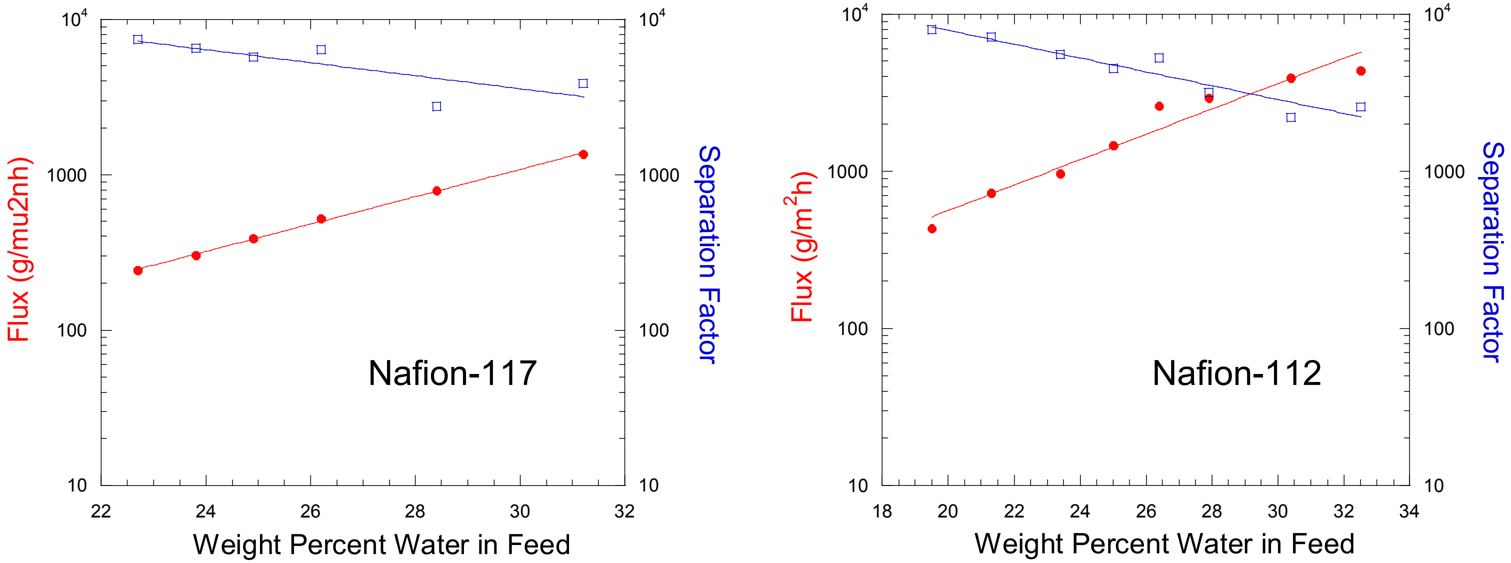
HI/iodine concentration



Flux (●) and separation factor (□) performance data for Nafion-117® (left) and Nafion-112® (right) at 134 ºC using an HI/water feed.

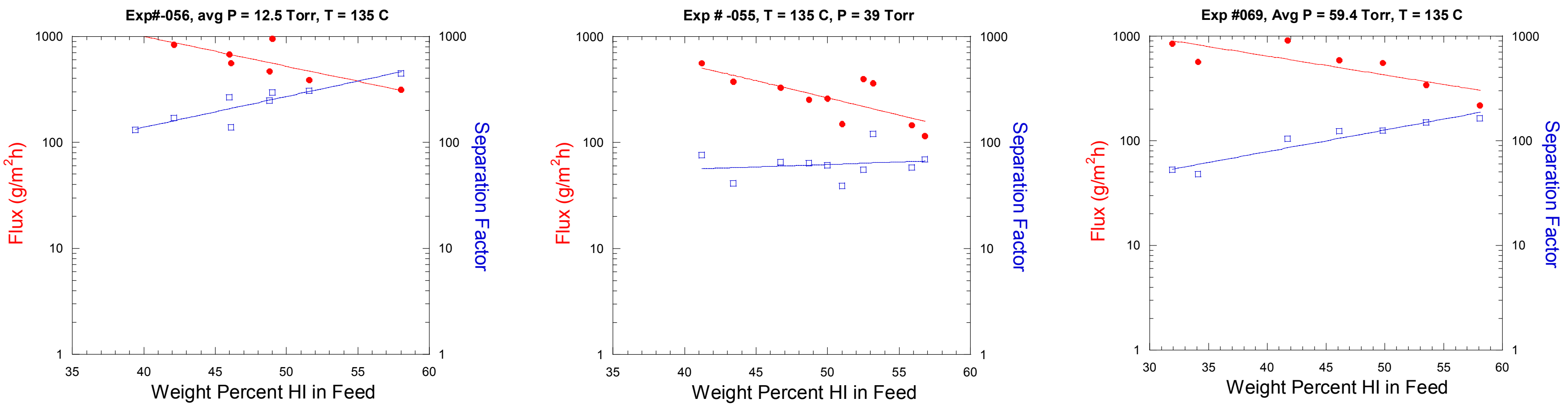
- **The addition of iodine to the feed results in a more corrosive fluid**
- **Solutions of HI/I_2/water were concentrated at 134 ºC without any significant degradation of the membrane**
- **Relative molar ratios in the feed: HI/I_2/water = 1/1/10**

What can we do with this data?

Relative measures of membrane performance as calculated at a 30 % HI feed concentration

Membrane	Feed	Flux (g/m^2h)	Separation Factor	Temp (ºC)	Membrane Thickness (μm)
Nafion-112®	HI	533	1007	134	50
Nafion-117®	HI	66	1870	134	180
SPEEK 1.7	HI	72	384	131	70
Nafion-112®	HI/iodine	3615	2857	134	50
Nafion-117®	HI/iodine	1082	3571	134	180

Newest work – Understanding the relationship between performance and driving force



- **From a process energy input perspective, the ΔP across the membrane (driving force) is a significant consideration**
- **Experiments have been performed at ΔP = 635, 608, and 588 Torr**
- **Separation factor lowers as the ΔP is reduced; however the separation factors are still substantial**
- **Flux is maintained**

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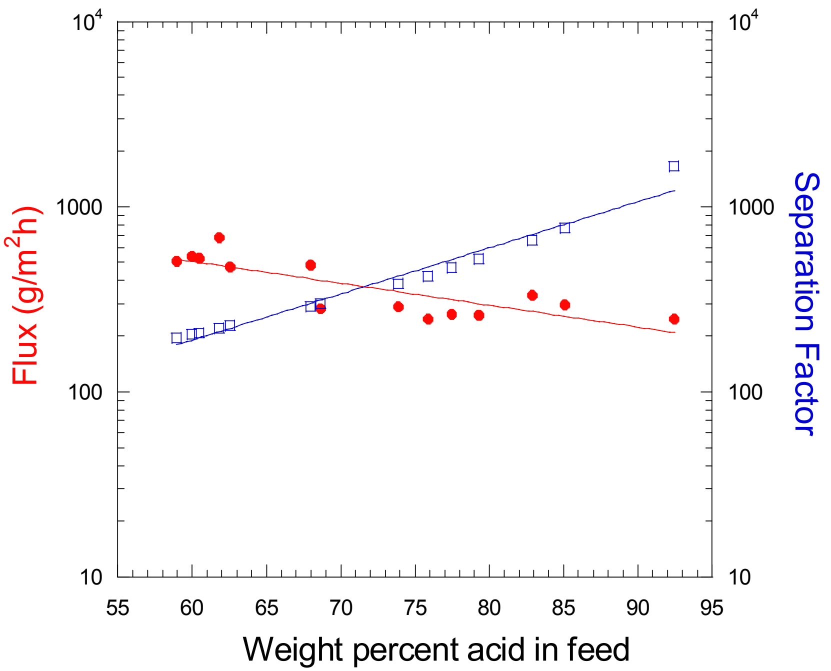
Sulfuric acid concentration



Sulfuric acid concentration data (flux [●] and separation factor [□]) for a Nafion-112® membrane at 100 ºC.

- Membrane: Nafion-112®
- Temperature: 100 ºC
- Pervaporation was used to increase concentration of sulfuric acid from 58% to 92%.
- No observed degradation of the membrane.
- Current experiments are being conducted at 120 ºC.
- Need to examine membrane performance as a function of backside pressure.

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Other identified separations

- H_2 from HI/I_2 after the HI decomposer – the reaction is equilibrium limited. To encourage higher conversion, removal of H_2 is warranted.
  - We have identified a series of polyimide membranes that are stable to 500 ºC that we have characterized for pure H_2 permeation.
- SO_2 from O_2 – separation of post-sulfuric acid decomposer products allows for SO_2 use in the Bunsen reaction
  - We have modeled the performance of over two dozen polymer materials for this separation and several offer outstanding performance and are chemically durable.

Future Work - Membranes

- FY 2007 work scope
  - Complete HI concentration experiments and collaborate with General Atomics for process modeling
  - Complete sulfuric acid separation characterization and collaborate with Sandia National Laboratory for process optimization
  - Upcoming key milestones
    - Determination of separations need for alternative chemical cycles (Draft report due 6/1/2007)
    - Final report on HI and sulfuric acid concentration (due 9/15/2007)
- FY 2008 Proposed work scope
  - Address remaining characterization work for sulfuric acid concentration
  - SO_2/O_2 membrane characterization (25 ºC, 5 Bar pressure)
  - H_2 separation from iodine and HI (300 ºC gas separation)
- Ultimate implementation of any membrane technology will be determined by INL and collaborators based upon best available laboratory data and focused process modeling. These activities will be performed in FY 2007 and FY 2008 as the relevant lab data becomes available.

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Summary

- **Relevance**
  - These projects are providing the enabling science and technology to make the S-I thermochemical cycle driven by nuclear energy an efficient reality
- **Approach**
  - Laboratory scale systems have been employed to characterize catalyst and membrane function
- **Technical accomplishments and Progress**
  - Pt/TiO_2 is an acceptable catalyst for the sulfuric acid decomposition reaction
  - HI can be decomposed over relatively stable activated carbon catalysts
  - Nafion membranes have been determined to be highly selective for water from both HI and sulfuric acid and are highly durable under extreme process conditions
  - Membranes have been identified for both $H_2/HI/I_2$ and SO_2/O_2 separations
- **Future work**
  - Development of catalysts with increased stability and low-temperature activity are needed for economic, long-term H_2 production by the S-I cycle
  - Complete membrane characterization and process modeling that will provide a basis of decision for inclusion of technologies in the S-I ILS